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Author(s) <u>Requested by Steve Wiley</u>

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From the first, sodium fluoride presented itself as the most logical intensifier because of the extremely powerful fluorescence produced in it by T, its negligible hygroscopic property, and the fact that it possesses only one crystalline modification under the experimental conditions. Furthermore, the only other element[3] that is known to cause similar fluorescence in sodium fluoride is columbium. It is reported[3] that the fluorescence is inhibited by TiO_2, SiO_2, sulfates and materials which form stable complexes with sodium fluoride or liberate HF. However, an excess of sodium fluoride will reduce such "quenching" of fluorescence to negligible proportions. Substances such as manganese and iron which absorb either the primary or secondary radiation will quench fluorescence; and several percent of calcium fluoride[4] in the sodium fluoride reduces the fluorescence greatly. A more detailed discussion of quenching effects will appear later in this report.

DISCUSSION OF EXPERIMENTAL WORK

The most obvious method of making semi-quantitative estimations of T by the fluorescence is to prepare a graded set of standard beads containing known amounts of T.[5] The brightness of a fluorescing bead containing an unknown amount of T can then be matched with the standards by direct visual comparison in ultra-violet light. In some instances it was found useful to wear glasses with yellowish-green lenses while matching the beads. By this method the amount of T on a bead could be determined to within a factor of five in the range 10^{-3} to 10^{-7} g of T per bead. For greatest accuracy in making these tests the beads had to be of nearly the same size, and only traces of impurities which colored the beads could be present. A mercury vapor lamp was used as the ultra-violet source, with several layers of

3. Papish and Hoag, Proc. Nat. Acad. Science 13, 726, 1927
4. Sandell, Colorimetric Det. of Traces of Metals, Interscience Pub. Co., N.Y. 1944, p. 434.
5. See Appendix A.

Corning, red-purple, Corex glass to filter out most of the visible light.

A simple instrument for obtaining quantitative measure of the relative intensity of fluorescence of two beads was constructed from a Duboscq Colorimeter (Cenco Catalogue #12352) and a small mercury vapor lamp with a purple filter (Fisher Catalogue #11-982 and #11-982-5). As can be seen in figures 1 and 2, the U.V. lamp is so placed that the light shines on the beads. Each bead is placed under a cylindrical prism of the colorimeter, and the path of the fluorescent radiation leads through an absorbing medium before reaching the cylindrical prism. In these experiments methylene blue was used as the absorbing medium. If the two semi-circular fields in the eyepiece, each receiving radiation from a different bead, are made to match in intensity, then the path length through the methylene blue solution of the light from the brighter bead will be the greater. The difference between these path lengths can be used to measure the relative intensity of fluorescence of the beads according to Beer's law:

(1) $\qquad \ln \dfrac{i}{nI} = kcl, \ n < 1$

Where nI is the fraction of the total intensity, I, of radiation from the fluorescent bead which enters the colorimeter, i is the intensity of radiation which has passed through a section of the methylene blue solution of length, l; c is the concentration of the methylene blue solution; and k is a constant.

When the semicircular fields are matched, $i_1 = i_2$, and

(2) $\quad \ln \dfrac{I_1}{I_2} = kc \ (l_1 - l_2) = K(l_1 - l_2)$

Experiments on several pairs of beads, in which for each pair the difference of the path lengths was constant for various values of the path lengths, proved that the instrument obeys equation (2) to a close approximation. The results of these experiments are given in Table I.

Table I

Data Shown That The Path Difference Is Constant for Given Pairs of Beads

Bead Pair	l_1	l_2	$l_1 - l_2$
1	4.2	0	4.2
	12.3	8	4.3
2	9.5	0	9.5
	18.6	8	10.6
3	3.1	0	3.1
	11.0	8	3.0
4	8.2	0	8.2
	16.7	8	8.7

Fortunately, the reading of a given comparison is independent of the intensity of the U.V. source. Consider the case where for a given I_1 and I_2 we have a certain l_1 and l_2. Then I_1/I_2 will be related to $(l_2 - l_1)$ by equation (2). Now if I_1 and I_2 are similar linear functions[6] of the incident U.V. intensity and the amount of active T per bead is independent of the U.V. intensity, then I_1/I_2 will be independent of the intensity and the readings l_1 and l_2 will not be affected by variations in the brightness of the U.V. lamp.

Even if the instrument measures relative intensity only approximately, this in no way limits its accuracy as an analytical tool; for the readings of 1 given by the instrument can be used to construct a curve from which the log of the amount of T in a bead can be read as a function of 1.

The instrument can be used for three different types of measurement:

6. Pringsheim and Vogel, Luminescence, Interscience, N.Y. (1943), p. 24.

First, the intensity of an unknown bead can be compared with the intensity of standard beads by merely placing the beads in the instrument and comparing the light field with both l_1 and l_2 set to zero. This is an approximate method.

The beads can be studied quantitatively by adjusting both l_1 and l_2 to match the fields for several sets of beads, and using equation (2) to refer the measured intensities to one standard bead. However, the best method, and the method by which the data in this report were obtained, is to compare a set of beads of graded intensity and known concentration with a standard bead of low intensity (containing approximately 10^{-8} to 10^{-7} g of T) and only adjusting the colorimeter cup on the side of the bead being compared. In this case l_2 is set equal to zero, and l_1 may be determined as a function of the amount of T per bead. This method is absolutely quantitative since the curve so constructed, of log (amount of T) vs. l_1, assumes nothing about relative intensity.

In all measurements it was found that a stock solution containing 0.323 g of methylene blue per liter, when diluted with water in the ratio of 1:7, gave the most satisfactory results as a light absorbing fluid.

In the preliminary studies of fluorescence a weighed amount of sodium fluoride was put into a little boat made by pressing a 1/4" hemispherical concavity in a platinum sheet. A drop of T solution was added from a calibrated micro-burette and the sodium fluoride was then fused to form a bead in the concavity. This method of bead formation was unsatisfactory for three reasons:

1. The platinum foil reflected a great amount of violet light.

2. The U.V. struck less than one-half of the bead.

3. The NaF-T melt collected at the edges of the boat during fusion.

We have found that the best method is to prepare beads on loops of #30 platinum wire, each loop being about 1.5 mm in diameter. At first the NaF was

weighed out very carefully, and fused into a bead. Later, however, the beads were formed by dipping the wire loops into NaF kept molten by a crucible furnace. If the loops were dipped, only once, thin flat beads weighing 1.7 $\pm$ .05 mg were formed. If the loops were dipped several times consecutively, larger beads could be built up weighing approximately 30 mg, but being by no means constant in weight. Although the flat beads have a reproducible weight, impurity effects are much magnified in such beads, and hence larger beads are to be preferred.

If the beads are transparent and we assume either spherical symmetry or small internal reflection, the geometry of the Duboscq instrument is such that two beads emitting the same amount of light but of somewhat different size will give the same reading when compared with a standard bead. If we then assume that the total intensity of fluorescence is a function of the number of "impurity centers" and does not depend on the distance between the centers, we must conclude that the reading of the instrument depends on the amount of T and not on its concentration in the sodium fluoride bead. This reasoning leads to the conclusion that the weight of the bead is not important as long as the beads are of approximately the same size. Within experimental error this seems to be true (see Table II), and therefore large beads made by dipping in molten NaF are to be preferred.

Table II

Fluorescence of Miscellaneous Sized Beads

	Amount of T per bead	Reading $(l_1$ when $l_2 = 0)$
Set 1	1.75×10^{-7} g	2.7
	1.75×10^{-7} g	2.9
	1.75×10^{-7} g	3.2
	1.75×10^{-6} g	10.7
	1.75×10^{-6} g	10.7
	1.75×10^{-6} g	10.1
	1.75×10^{-5} g	18.6)
	1.75×10^{-5} g	20.4) Deviation will
	1.75×10^{-5} g	21.8) be explained.

Table II (cont.)

Set 2	Amount T per Bead	Reading $(i_1$ when $i_2 = 0)$
	1.75×10^{-7} g	2.9
	1.75×10^{-7} g	2.7
	1.75×10^{-7} g	2.9
	1.75×10^{-6} g	11.0
	1.75×10^{-6} g	12.9
	1.75×10^{-6} g	12.6
	1.75×10^{-5} g	19.5)
	1.75×10^{-5} g	21.6) Deviation will
	1.75×10^{-5} g	20.4) be explained

The sodium fluoride used for bead preparation fluoresced before any T had been added. This "background" fluorescence varied from melt to melt; and to obtain reliable analytical results it was necessary to fashion the beads used in a given analysis from the same melt that the standard beads used in constructing the curve were made. This is an extremely important point, and failure to take heed of it can lead to erroneous analytical results.

Since the sensitivity of the test increases with a lowering of background fluorescence, some so-called "non-fluorescent" NaF (NaF having a low background) was made[7] by crushing the fused salt, and picking out the more fluorescent crystalline fragments by hand.

Sodium fluoride formed from HF and Na_2CO_3 showed a rather high background fluorescence. If the proper quenching agent were found it seemed feasible to produce beads with a low background by adding just enough quenching agent to inhibit the background fluorescence. However, experiments using various quenchers proved unsuccessful.

It was advisable to coat the standard beads, which were used as comparison beads in the instrument, with a solution of cellulose esters in acetone. This protected them from wear and dirt.

7. See Appendix B.

The quenching effects of various agents were tested by preparing beads containing 1.75×10^{-7} g T each, and observing whether or not the intensity of fluorescence was diminished by addition of those agents to the beads.

Table III sums up all the data obtained in this study.

Table III

Effect of Impurities on the Fluorescent Beads

Agent	Amount per Bead	Results
NaCl	ca 10^{-2} g	No effect
SO$_4$	1.59×10^{-4} g	No effect
KMnO$_4$	7×10^{-3} g	Coating of opaque black MnO$_2$ formed on bead surface.
Fe	4.75×10^{-6} g	Quenching by absorption of U.V.
Sn	Large amount	Quenching
Hg	" "	Volatilizes and thus does not quench
Mn	" "	Quenching
Cr	" "	"
Co	" "	"
Ni	" "	"
Cu	" "	"

The best range for analysis (it being understood that there must be some flexibility to handle the effect of varying background fluorescence) was found to be the interval between 10^{-8} and 5×10^{-6} g of T per bead. In this range, as the experimental graph in figure 3 indicates, the intensity of fluorescence is approximately a linear function of the amount of T present in the bead.

With concentrations above 5×10^{-6} g of T per bead, black specks of T_3O_8 formed during fusion begin to appear on the bead surface. This obviously makes measurements above this limiting value unreliable, since only the TO_2^{+4} in the lattice is responsible for the fluorescent radiation. The irreproducibility of the data in Table II for the beads containing 1.75×10^{-5} g T is caused by this oxidation of T; for black specks could be seen on these beads. Some authors[8] speak of the intensity vs. concentration curve passing through a maximum. We have added T in amounts as high as 2×10^{-4} g per bead, and have observed a diminution of fluorescence. However, since large black areas of T_3O_8 were apparent on the bead surface, there was no reason to believe that the diminution was not purely a result of the obstruction to radiation furnished by the opaque T_3O_8.

The lower limit of the analytical range is imposed by the back ground fluorescence, and its magnitude can vary with this fluorescence.

Because of the obvious quenching effects of the various common impurities, schemes of separation suitable to this type of analysis were necessary. In all our endeavors in this field we tried to avoid tedious and costly chemical procedures, and have favored physical processes.

An interesting series of experiments were carried out by permitting the impure T solution to diffuse along standard strips of filter paper impregnated with NaF. When these strips were dried it was observed that all colored impurities such as iron, nickel, copper, and manganese diffused about half as rapidly as the aqueous solvent, being preferentially absorbed by the porous medium. When such a strip was subjected to U.V. radiation, a rather intensely fluorescent band was observed along the boundary which marked the limiting height of aqueous diffusion.

8. See Reference 2: also Pringsheim and Vogel, ref. cit., p. 26.

At first, it was thought that this might be an excellent method for the separation and analysis of T. However, it soon became apparent that difficulties existed since the width and brightness of the fluorescent band did not change when the concentration of the tubanyl ion was varied from about zero (distilled water) to 10^{-2} g T per cc. It seemed that the fluorescent band was formed by a concentration of activating impurities from the sodium fluoride, which exhibited a rather high background when fused into a bead. This idea is supported by an experiment in which distilled water was allowed to diffuse up the unimpregnated part of a strip of filter paper, only half of which was filled with sodium fluoride. When the water reached a point slightly inside of the impregnated area, the strip was dried, and no fluorescent band could be observed. Since impurities in the sodium fluoride were not leached out and carried along by the diffusing water in this case, a fluorescent band would not be expected to be found unless the activating impurities came from the water or the filter paper itself. If the fluorescent spectrum of those bands is the same as that of tubanyl activated sodium fluoride, more work will be done on this method. This might prove to be a rapid semi-quantitative way of determining T if non-fluorescent sodium fluoride were used.

Electrolysis with a mercury cathode[9] is very successful in removing many impurities which interfere with the fluorescent method of analysis. Nitrate ion was destroyed by reduction with formic acid[10] before electrolysis; and after electrolysis the T was put into the form of tubanyl nitrate by fuming with nitric acid. A drop of the tubanyl solution was then fused into a sodium fluoride bead. As can be seen in the following table, this method of purification is very successful. Moreover, in the case (sample III) where the method failed it was apparent that there was quenching since the center of the bead did not glow

9. See Appendix C for a description of this method. Pavlish and Sullivan, Met. and Alloys, 11, 56, (1940)

10. Kunderman and Tolbert, Chem. Report S-266 (UCRL)

as brightly as the rest of it.

Table IV

Fluorescence Analysis After Electrolysis

Sample	Amount of T by Fluorescence Analysis

I. Containing

    10 g Fe per liter
    10 g Cu per liter   10 mg T per liter
    10 g Ni per liter
    10.2 mg T per liter

II. Containing 4.31 liters

0.083 g Li	0.008 g Gd
0.34 B	0.067 g Sm
4.5 Mn	0.1 g Be
2.0 Co	50.0 g Fe
1.5 Ag	10.0 g Cr
0.42 Cd	5.0 g Ni
1.62 Nd	498. g Cu

with 11.6 gm T per liter

                                         11.5 gm T per liter

III. A natural sample found to contain about 5 ppm of T by alpha count. This material was a sludge of salts.

                          0.56 ppm
                (Definitely low because of quenching)

IV. A natural sample found to contain about 15 ppm of T by alpha count. This material was a thick sludge.

                          7.ppm
            (Very slight quenching if any; error possibly in alpha count.)

The urine of two individuals who had been exposed to large amounts of T was also examined by the fluorescence method. Organic matter was removed by ignition and HNO_3 was added to reconvert any T_3O_8 to TO_2^{++}. The residue did not cause fluorescence in a bead and it also appeared that the background fluorescence of the sodium fluoride was paritally quenched. Perhaps a combination of electrolysis with a succeeding distillation of TCl_4[11] from the impurities not removed in the electrolytic process would serve to purify any type of material containing T so that a fluorescence analysis could be performed. We are contemplating a study of such a procedure.

11. Maier, Bur. Mines Tech. Bull. 360, 1, (1925)

APPENDIX A

The Preparation of Standard Beads

C.P. sodium fluoride was put into a medium sized platinum dish which was then placed in a crucible furnace, and maintained at a temperature of about 1200°C.

Clean platinum loops (without handles of glass or any other material) were then dipped repeatedly until a bead weighing about 30 mg was produced. The loops (#30 wire) had diameters of approximately 1.5 mm and were held, during dipping, by a long forceps which was locked by a wire band.

The beads were placed in a little wooden stand in which holes were drilled to accommodate the wire ends. All handling was carried out with a small pointed forceps, and the stand was then placed under a bell jar.

From a calibrated micro-burette, drops of Tubanyl solutions were added to a series of beads. These drops were carefully dried, caution being taken to prevent spattering, and the residues were fused into the beads in a Bunsen flame.

In all steps before the final fusion, the beads were kept covered by the bell jar as much as possible because contamination before fusion is a serious affair, whereas after fusion, contamination cannot do much harm.

All apparatus was carefully cleaned with warm nitric acid before any of the above procedure was carried out.

APPENDIX B

The Preparation of Sodium Fluoride with Low Background Fluorescence

C.P. sodium fluoride was placed in a platinum dish and fused in a crucible furnace. The fused mass was then dumped on a clean glass plate and broken up. The fragments were viewed under ultra-violet light and those which contained fluorescent specks were removed with the aid of a clean forceps. The remaining crystals were each broken into quarters and the selection process was repeated on these pieces. The remaining sodium fluoride was fused again, and the crystalline fragments of this latter fused mass were observed to be free of fluorescent specks and to possess a rather low background fluorescence. Before use all the apparatus for the above procedure was carefully cleaned in warm HNO_3 and the material was protected from contamination by dust in the air.

APPENDIX C

Methods of Bead Analysis

An aliquot portion of the solution to be analysed was placed in a clean beaker and warmed on a hot plate. One cc of H_2SO_4 (conc.) was added for every 25 cc of solution. Thirty drops of formic acid were than permitted to run into the beaker from a dropping funnel. When brown fumes (nitrogen dioxide) began to be evolved, dropping was continued at the rate of one drop per second until the fumes ceased to come off. This indicated that nitrates had been satisfactorily destroyed.

The solution was then transferred to an electrolysis cell with a mercury cathode, and electrolyzed by a current of five to seven amps under a potential difference of twelve volts. These conditions were obtained by adjustment of the cell resistance with H_2SO_4.

The electrolysis was continued for several hours after an iron test (SON) was negative. Then the solution was filtered, and evaporated to dryness on the hot plate to remove sulfuric acid. The residue was taken up in aqueous HNO_3 and warmed for awhile to assure that all the T was in the form of TO_2^{++}. Then an aliquot portion of this final solution was added to a bead by means of a micro-burette. The aliquot was adjusted so that the bead contained about 6×10^{-7} grams of T. This represents a good condition, so far as intensity is concerned, for fluorescent analysis.

All apparatus was cleaned with warm HNO_3.

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Figure I

An Instrument for Fluorescence Analysis

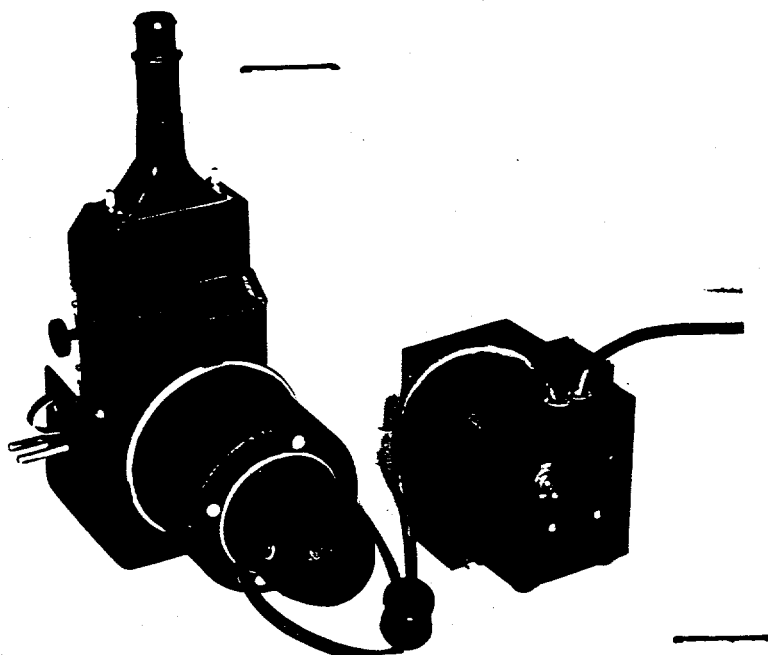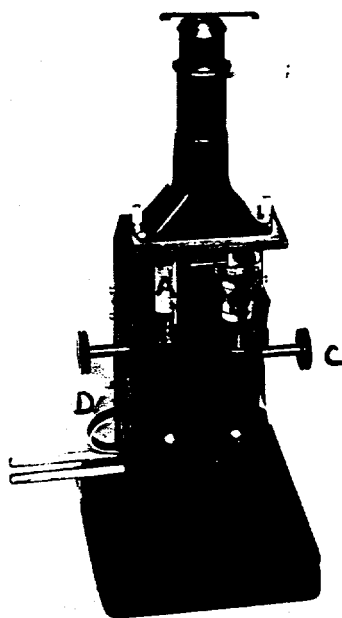## Figure II

The Instrument with the Cover and U.V.
Lamp Removed

A. Cylindrical Prism
B. Cup of methylene blue solution
C   Knob to adjust the height of the cup
D. Sliding tray with clamps to hold beads
E. Fluorescent bead

FIGURE III

These points
are unreliable
because of oxide formation

Log of the am't of T in grams per bead

Reading